

Predicting d^0 magnetism

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Predicting magnetism originating from $2p$ orbitals is a delicate problem, which depends on the subtle interplay between covalency and Hund's coupling. Calculations based on density functional theory and the local spin density approximation fail in two remarkably different ways. On the one hand the excessive delocalization of spin-polarized holes leads to half-metallic ground states and the expectation of room temperature ferromagnetism. On the other hand, in some cases a magnetic ground state may not be predicted at all. We demonstrate that a simple self-interaction correction scheme modifies both these situations via an enhanced localization of the holes responsible for the magnetism and possibly Jahn-Teller distortion. In both cases the ground state becomes insulating and the magnetic coupling between the impurities weak.

Conventional magnetism is associated with a narrow region of the periodic table, namely that of the $3d$ and $5f$ series. In these atomic shells strong Hund's coupling results in a high-spin configuration and therefore in the formation of localized magnetic moments. Then one also needs a mechanism for coupling those local moments. This is not universal and generally depends on the details of the compound investigated. Importantly the formation of magnetic moments does *not* imply a macroscopic magnetic state. Furthermore, the orbital composition of the moment is crucial for establishing the microscopic nature of the coupling mechanism.

Following the criterion of having large Hund's coupling one should expect to find high-spin configurations and possibly magnetism also in materials with partially filled $2p$ orbitals. This situation takes the name of d^0 magnetism¹. Oxygen is the prototypical case: O_2 has a triplet ground state and solid O orders in a complex antiferromagnetic structure at low temperature². Another remarkable example is that of Rb_4O_6 , which was predicted to be an anionogenic half-metal³, and measured spin-glass⁴. Away from molecular solids however the situation is less clear. Two properties of standard solids conspire against p -type magnetism. First, the p shells are usually fully filled and therefore cannot sustain a magnetic moment. Secondly the $2p$ hopping integrals are usually large and so are the typical bandwidths, meaning that the chances of moment formation are reduced by the large kinetic energy.

Despite these complications the experimental claims for d^0 ferromagnetism are numerous and include graphitic carbon⁵ and both defective⁶ and doped oxides⁷. An explanation of these findings however remains controversial to date. The formation of the magnetic moment is usually attributed to holes localized at the defect site, either this being the molecular orbital associated to cation vacancies^{8,9} or p -dopants at the O sites^{10,11}. Then the magnetic coupling is justified with the degree of delocalization of the same $2p$ shell responsible for the moment, in a scheme similar to the Zener model for standard magnetic semiconductors¹². Critically most of the predictions are based on density functional theory (DFT) using local approximations of the exchange correlation

potential (LSDA or GGA). These notoriously underestimate Coulomb repulsion and tend to over-delocalize the charge density. It is then no surprise that most of the calculations return a metallic (half-metallic) ground state and usually extremely large magnetic interaction.

In this letter we demonstrate that, when strong correlation is introduced at the level of self-interaction correction (SIC) the picture changes drastically and even the formation of a local moment becomes a delicate issue. Consequently the mechanism for magnetic interaction can be completely different from that described by the LSDA. We prove this idea by presenting three prototypical cases. First we look at F centers in SiO_2 for which LSDA predicts a delocalized hole sustaining magnetic interaction instead of a paramagnetic self-trapped center^{13,14}. Then we look at B, C and N substituting for O in MgO , for which LSDA correctly predicts a magnetic ground state but fails in capturing the orbital order and the insulating state. Finally we look at the case of Ga vacancy and dopant Zn in GaN. The former case is similar to that of F centers in SiO_2 while in the latter, LSDA now fails in predicting a high-spin state.

Our calculations are performed using the standard DFT code SIESTA with LSDA functional¹⁵ and a development version implementing the atomic SIC scheme (ASIC)¹⁶. We treat core electrons with norm-conserving Troullier-Martin pseudopotentials, while the valence charge density and all the operators are expanded over a numerical orbital basis set, including multiple- ζ and polarized functions¹⁵. The real space grid has an equivalent cutoff larger than 500 Ry. Calculations are performed with supercells of various sizes including k -point sampling over at least 10 points in the Brillouin zone. Relaxations are performed with standard conjugate gradients until the forces are smaller than 0.04 eV/Å.

We begin our analysis by considering the famous prototypical case of the F center in SiO_2 , i.e. Al substituting Si (Al_{Si}). In table I we summarize the results of our LSDA and ASIC calculations. These have been obtained with a 36 atom unit cell containing a single Al impurity. The LSDA local geometry of Al_{Si} has the four Al-O bonds of equal length, 1.73 Å, and the $S=1/2$ hole spreads uniformly over the four O atoms. However relax-

System	d_{LSDA}	μ_{LSDA}	d_{ASIC}	μ_{ASIC}
SiO ₂ : Al _{Si}	1.73 (4)	1	1.67 (3), 1.94 (1)	1
MgO: B _O	2.19 (6)	3	2.20 (6)	3
MgO: C _O	2.18 (2), 2.15 (4)	2	2.18 (4), 2.15 (2)	2
MgO: N _O	2.10 (6)	1	2.15 (4), 2.10 (2)	1
GaN: V _{Ga}	2.10 (4)	3	2.14 (2), 2.28, 2.31	3
GaN: Zn _{Ga}	2.0 (4)	0	1.96 (3), 2.4 (1)	1

TABLE I: Summary table of the LSDA and ASIC calculated bond lengths, d (in Å), and magnetic moments, μ (in μ_B), for the various defects investigated in SiO₂, MgO and GaN. In bracket the number of bonds of a given length.

ation with ASIC produces a distortion. Three of the Al-O bonds relax to 1.67 Å, while the forth gets considerably longer (1.94 Å). Such a distortion is associated with the localization of the Al-induced hole, which occupies the orbital along the elongated bond. This picture is consistent with the experimentally found hole self-trapping and demonstrates the importance of SIC in the self-trapping problem¹⁴.

If one now calculates the magnetic interaction between two Al_{Si}, a remarkable result is found. By using a 72 atom supercell containing two Al impurities placed at second nearest neighbours, we have calculated the energy difference, ΔE , between the ferromagnetic and antiferromagnetic configurations of the cell. This is about 120 meV for LSDA meaning that for Al concentrations around 8 % LSDA predicts SiO₂:Al to be a ferromagnet with an estimated mean-field critical temperature of 240 K. No magnetism has ever been reported for SiO₂:Al at any concentrations and we conclude that this is simply an artifact of the excessive LSDA hole delocalization. When the same calculation is repeated with ASIC we find that the total energy difference drops to 1 meV, i.e. it is consistent with no magnetic coupling. These results set the theoretical benchmark of our method.

Next we analyze the case of O substitutional defects A_O (A = B, C, N), in rock-salt MgO. These introduce respectively 3, 2 and 1 hole, so that the filling of the A_O 2*p* shell is respectively 1/2, 2/3 and 5/6. In figure 1 we report the density of states for a 96 atom supercell doped with a single A_O and projected over the A_O 2*p* orbitals. For all the impurities both the LSDA and ASIC return a spin-polarized ground-state with a magnetic moment as large as the number of holes. The details of the charge distribution around A_O are however profoundly different in LSDA and ASIC.

Let us look at the single acceptor N_O first. A magnetic ground state means that the hole is fully spin-polarized. The problem is then that of distributing a single hole among the three 2*p*-orbitals forming the chemical bonds with the Mg cations. As for SiO₂ also in this case LSDA predicts a spin-polarized ground state with the Fermi level cutting across a 2/3 filled minority N-2*p* impurity band. LSDA atomic relaxation is isotropic with a N-Mg

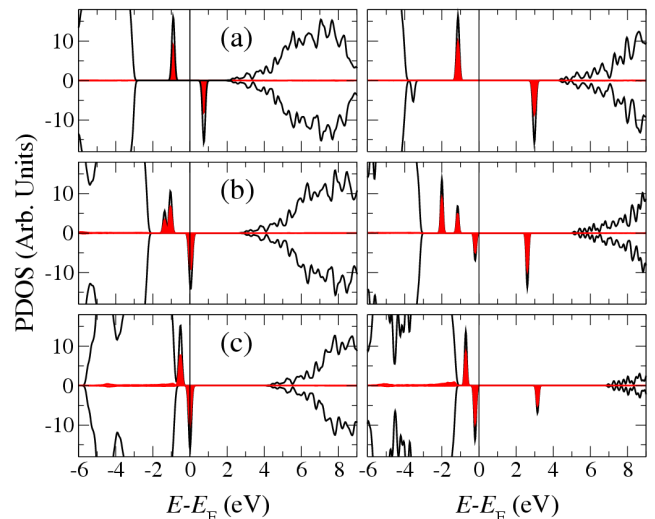


FIG. 1: (Color on line) Total density of states (black line) and density of states projected over the 2*p* shells of the anion acceptor (red line) for MgO doped respectively with B (a), C (b) and N (c). The left-hand (right-hand) side plots correspond to LSDA (ASIC). The majority (minority) DOS is plotted in the upper (lower) half of each panel.

bond-length slightly larger (2.10 Å) than that between O and Mg of 2.08 Å. This half-metallic ground state, together with the considerable energy overlap between the O 2*p* and N 2*p* orbitals (see Fig.1), is suggestive of a N ferromagnetic order via an impurity band Zener mechanism. In fact the calculated ΔE for a 96 atom cell and second nearest neighbours is 120 meV and ferromagnetic.

Note however that this partially filled degenerate *p* configuration is sensitive to Jahn-Teller distortion. This is not captured by LSDA, due to the erroneous over-delocalization of the hole, but it can be described by an ASIC calculation. ASIC in fact leads to the expansion of the two of six N-Mg bonds (2.15 Å) with the consequent N-2*p* levels splitting into a doubly degenerate occupied level just above the MgO valence band and an empty singlet. These are separated by a crystal field energy of approximately 3 eV. In this distorted configuration the magnetic moment is entirely localized over the longer of the *p* bonds as it can be clearly seen from Fig. 2 where we present the ASIC magnetization isosurface.

As it is, MgO:N is an insulator and the only mechanism left for magnetic coupling between N_O is superexchange. This is expected to be extremely weak, since the first available Mg filled shells to mediate the virtual transition necessary for superexchange are the 2*p*, which are extremely deep, leading practically to no coupling. In fact the calculated coupling at second nearest neighbour is only 1 meV. Note also that, at variance to the standard Jahn-Teller distortion for *d* orbitals, the *p*-type distortion investigated here is frustrated, and each of the three degenerate 2*p* orbitals can transform into the singlet. This introduces an additional complication to the

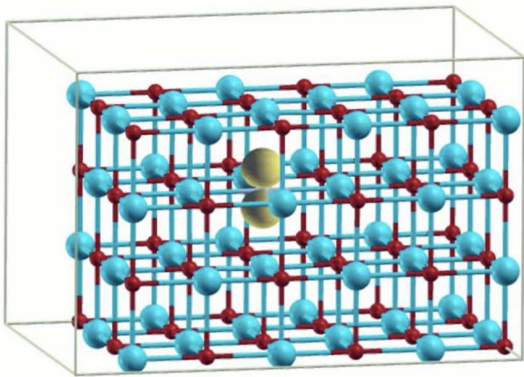


FIG. 2: (Color on line) Magnetization isosurfaces calculated with ASIC for N_O in MgO. Note that the $S=1/2$ hole is completely localized along the p_y orbital and it is not evenly distributed along all the bonds. Color code: blue=Mg, red=O, N is not displayed for clarity.

superexchange mechanism, since only orbitals sharing the same angular momentum about the bonding axis can participate to the coupling. Finally we note that a similar Jahn-Teller distortion was predicted by Elfimov et al.¹⁸ for N-doped SrO.

Let us now move to $MgO:C$. This time the minority C- $2p$ shell is singly occupied leading to a magnetic moment of $2 \mu_B$ for both LSDA and ASIC. For C_O also LSDA predicts Jahn-Teller distortion with four 2.15 Å and two 2.18 Å long Mg-C bonds. One hole distributes entirely over the $2p$ orbital associated to the long bond but the second spreads evenly over the remaining orbitals again giving a half-metallic ground state (Fig.1b). ASIC changes the Jahn-Teller distortion into two short (2.15 Å) and four long (2.18 Å) bonds, basically reversing the LSDA geometry. In addition ASIC correctly describes the level occupation giving a filled singlet (shorter bond) separated by about 2.5 eV from an empty doublet.

The triple acceptor B_O presents a somewhat less critical situation. Now the B $2p$ impurity band is half-filled and positioned completely within the MgO band-gap. The strong Hund's interaction produces a magnetic ground state with a magnetic moment of $3 \mu_B/B$ for both LSDA and ASIC. For such an occupation the Jahn-Teller mechanism does not operate and the LSDA and ASIC bandstructures are qualitatively similar.

When we look at the magnetic coupling we find for both N and C a situation very similar to that of Al in SiO_2 , i.e. a large magnetic coupling in LSDA and practically no coupling in ASIC. The situation is rather different for B where even LSDA does not predict magnetic coupling. Does this mean that ferromagnetism cannot exist in these compounds? The answer to this question is not simple and essentially relates to the behaviour of the impurities with additional doping. For instance by adding a fractional electronic charge to C_O one should find a situation intermediate between that on C_O and N_O . Such a charge however feels a weaker nuclear poten-

tial and certainly localizes less. Although it is likely that it will occupy one of the empty C_O p orbitals, leading once again to a half-metallic band-structure, the quantitative details of its exact localization are not easy to predict. Since the ferromagnetism is the results of the subtle interplay between localization, necessary for the magnetic moment formation, and de-localization, necessary for the magnetic coupling, we believe that a more accurate electronic structure method capable of taking all these factors into account is needed.

We finally move our attention to Ga vacancy (V_{Ga}) and of Zn substitutional for Ga (Zn_{Ga}) in GaN. The first is again a triple acceptor and it was recently proposed as possible source of d^0 ferromagnetism¹⁹, while the second introduces only one hole, which is predicted non-magnetic by LSDA. Our results, obtained with a 64 atoms supercell are summarized again in table I, where we can observe that LSDA and ASIC agree on the magnetic ground state of V_{Ga} , but give respectively a non-magnetic and a magnetic $S=1/2$ state for Zn_{Ga} . The non-magnetic state found in LSDA is resistant to supercell size and persists to cells as large as 256 atoms, which are already large enough to decouple the impurities located in the periodic mirror cells.

Let us consider first the case of V_{Ga} . Here the situation is somehow similar to that of $MgO:N$, where the magnetic state is reproduced already at the level of LSDA, but the spatial distribution of the moment changes radically when SIC is considered. In LSDA, in fact, the four N surrounding the vacancy move outwards so that the distance with the vacant site is 2.1 Å, about 8% longer than that between Ga and N. Such displacement is isotropic and the three holes spread uniformly over the four available bond directions of the wurtzite lattice (see figure 3). Thus the material turns out to be half metallic¹⁹. The ASIC picture is however rather different. Also in this case the SIC allows the hole to be localized. The ASIC relaxation leads to two bonds of 2.14 Å and two longer of bonds of slightly different lengths. The longest of the four is fully filled and the three holes localize on the remaining three (Fig. 3). Such a situation reminds that of Al_{Si} and it is a further demonstration of the effects of self-trapping. Also for $GaN:V_{Ga}$ self-trapping massively suppresses the magnetic coupling energy which reduces from 145 meV (antiferromagnetic) in LSDA (for two V_{Ga} placed at 6.3 Å from each other), to 1 meV for ASIC.

The situation for the single acceptor Zn_{Ga} is dramatically different with LSDA giving a non-magnetic ground state with the hole evenly distributed over the four almost tetrahedrally coordinated bonds. These are just slightly expanded to about 2 Å. ASIC again captures the Jahn-Teller distortion: three Zn-N bonds re-adjust to a distance of 1.96 Å, while the forth expands considerably to 2.4 Å. The hole now completely localizes over the longest bond, and due to the enhanced degree of localization Hund's coupling spin splits the energy level in forming a spin 1/2 ground state. The ASIC electronic structure then is that of Zn_{Ga} being a paramagnetic deep

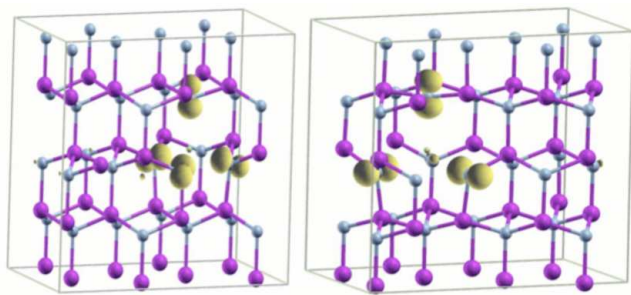


FIG. 3: (Color on line) Isosurface of the 3 holes (the magnetization) associated to V_{Ga} in GaN as calculated with LSDA (left) and ASIC (right). In LSDA the holes are distributed uniformly over all the four N ions surrounding the vacancy, while they localize around the longer three bonds in ASIC.

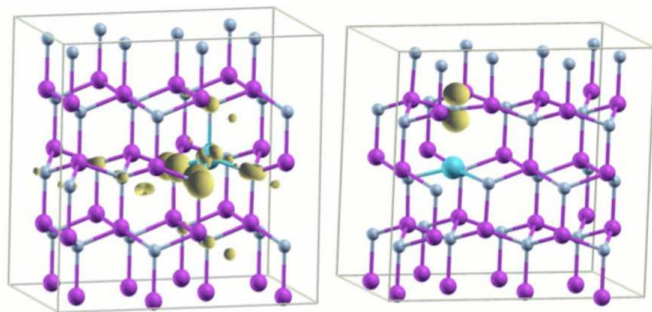


FIG. 4: (Color on line) Isosurface of the hole (the magnetization) associated to Zn_{Ga} in GaN as calculated with LSDA (left) and ASIC (right). In LSDA the hole is unpolarized and distributed uniformly over all the four N ions surrounding the vacancy, while it spin-splits and localizes around the longer bond in ASIC.

trap instead of a shallow non-magnetic acceptor.

In conclusion we have demonstrated that the problem of predicting the magnetic ground state of p -type impurities is an extremely delicate one. In general standard LSDA is unable to capture Jahn-Teller distortion and systematically underestimates the electron localization. As a consequence Hund's coupling is also underestimated. In the best case scenario a magnetic ground state is still predicted, but the spatial distribution of the magnetic moment is inaccurate. This typically leads to a metallic (via impurity band) ground state, strong exchange coupling between the magnetic impurities, and the expectation of room temperature ferromagnetism. The removal of the self-interaction error results in Jahn-Teller distortion and the creation of insulating ground state with little to no magnetic coupling between the impurities. A more drastic situation is however encountered when the erroneous LSDA delocalization strongly suppresses Hund's coupling and produces a non-magnetic ground state. Also in this case ASIC is able to fix the problem and predicts non-vanishing magnetic moment localized at distorted bonds.

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